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54 **Solid glyphosate compositions and their use.**

57 A solid phytoactive composition comprising:

- a) N-phosphonomethylglycine in the form of a salt or the free acid;
- b) an alkyl glycoside or alkyl polyglycoside; and
- c) an agriculturally acceptable inorganic ammonium salt, preferably ammonium sulfate.

EP 0 498 145 A1

Background of the invention

The present invention relates to solid phytoactive glyphosate formulations and their use to kill and control unwanted vegetation.

5 Glyphosate (N-phosphonomethylglycine) and its salts are well known phytoactive compounds, and the monoisopropylamine salt of glyphosate is present in a well known commercial phytoactive formulation sold under the registered trademark ROUNDUP.

In the present specification and claims, phytoactive means effective as a plant growth regulator, as a herbicide or a defoliant.

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Description of the prior art

Stauffer Chemical Company's European Patent Application No. 0 220 902 discloses a liquid phytoactive composition and methods of use thereof, comprising an N-phosphonomethyl-N-carboxymethyl compound, one or more liquid nonionic surfactants, more particularly alkyl polyglycosides, a dispersing medium or solvent for the N-phosphonomethyl-N-carboxymethyl compound, and one or more inert adjuvants, such as for instance antifoaming agents, thickener, etc. This composition is said to be particularly advantageous and to offer the property of being minimally irritable to the eyes and of being less toxic in view of the use of a surfactant derived from a naturally occurring product.

20 ICI Australia's European Patent Application 0 264 202 discloses that alkyl glucoside surfactants having an alkyl:glucose ratio of about 1:1.4 can be used in combination with N-phosphonomethylglycine in order to produce a herbicidal composition especially useful for killing grass weeds. The formulations disclosed are aqueous solutions.

25 Purpose of the invention

The present invention provides a new solid phytoactive glyphosate composition providing the advantage of saving storage place, lowering transportation costs, containing a high active ingredient content and providing good phytoactivity with that of low toxicity with respect to the environment.

30 Another aspect of the invention is concerned with the enhancement of glyphosate activity in the presence of an alkyl polyglycoside surfactant and ammonium sulphate.

It is known that ammonium sulphate can enhance the herbicidal activity of glyphosate, but if, as usual, the spray solution contains a surfactant, the effect of ammonium sulphate is markedly dependent on the type of surfactant. For example, Turner and Loader, Weed Research 1980 (20), 139-146, report the results of studies with various surfactants. They found that when used without ammonium sulphate, relatively hydrophilic nonionic or cationic surfactants provided glyphosate formulations having higher unit herbicidal activity. In the presence of ammonium sulphate, however, more hydrophobic (lipophilic) surfactants gave superior results than when using these surfactants alone. With or without ammonium sulphate, cationic surfactants such as ethoxylated fatty amines, provided more effective herbicidal spray solutions than nonionic surfactants such as nonylphenol ethoxylates (see EP-A-0 290 416).

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Essential characteristics of the invention

According to the present invention, the new solid composition as disclosed hereafter shows particular advantages in treating grassy weeds.

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The solid composition of the invention comprises:

- a) N-phosphonomethylglycine in the form of a salt or the free acid;
- b) a surfactant comprising an alkyl glycoside or alkyl polyglycoside; and
- c) an agriculturally acceptable inorganic ammonium salt, preferably ammonium sulfate.

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It is known that use of alkyl glycosides or alkyl polyglycosides as surfactant provides due enhancement to the phytoactivity of a glyphosate compound. But, in applicant's invention, the combination of an ammonium salt with alkyl polyglycosides enhances the phytoactivity of the glyphosate in a notably, non-expected manner. Moreover, the above formulation as a solid further enhances this invention.

Furthermore, the solid composition of the invention can have a high active ingredient content. Another advantage is that the composition of the invention may be packaged in disposable containers or recyclable containers.

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In compositions in which the combined weight of the glyphosate and alkyl polyglycoside provides more than about 80% of the total weight of the composition, the ratio by weight of the glyphosate acid equivalent

to alkyl polyglycoside is usually at least 4:1, and is preferably at least 4.5:1, for example from 5:1 to 10:1.

In compositions containing a significant amount, for example at least 50% of the total weight of the composition, of a water-soluble carrier, the ratio by weight of glyphosate acid equivalent to alkyl polyglycoside can be, for example, from 1:1 to 10:1.

5 In compositions containing in the range from about 20 to about 50% of the total weight of the composition, of a water soluble carrier, the ratio by weight of glyphosate acid equivalent to alkyl polyglycoside can be from about 1/1 to about 5/1.

The alkyl glycosides or alkyl polyglycosides for use in the present invention may be obtained by the reaction of alkanols with glucose or other monosaccharides, or with disaccharides, for example sucrose, or with polysaccharides. Surfactants prepared from mixtures of monosaccharides and disaccharides as well as from mixtures of alkanols can be used. For example certain commercially available alkyl glycosides are products of the reaction of glucose with a mixture of alkanols containing 8 to 10 carbon atoms. The number of alkyl groups per saccharide molecule can vary; for instance mono- or dialkyl glucose or sucrose derivatives are possible.

15 Preferably, the following surfactants are used in this invention, identified by their trade name: Atplus 450, Triton BG-10, Atplus 258, APG 300 (Henkel), alone or in combination with one another or with other surfactants, preferably surfactants showing good compatibility properties with the alkyl(poly) glycoside used and the glyphosate constituent as well as low toxicity properties according to standard tests. As a preferred class one may employ alkoxylated sorbitan fatty acid esters, quaternary ammonium surfactants, preferably propoxylated ammonium surfactants, or other amine surfactants.

As inerts, one may suitably use defoamers known per se in the art which may be liquid or solid. Alkyl polyglycoside surfactants foam, particularly when used with water in a spray tank, and therefore generally require a defoamer. In liquid formulations containing glyphosate, the defoamer often easily separates out from the liquid medium, thus creating stability and long storage problems. However, when a defoamer is present in our solid composition according to the invention a liquid composition prepared therefrom does not separate out. Our solid composition does not have stability problems or long term storage problems.

Further, due to the separation of the defoamer from the liquid medium in a case of liquid formulation of the prior art, that liquid composition has to be shaken before use; which requires packaging in small containers. However, dry formulations according to the present invention can be packaged in large quantities at relatively low cost.

The solid composition according to the present invention may still contain up to 10% by weight of water; preferably, however, the water content should not be more than about 8% depending on the amount of other liquid components of the dry solid composition.

The active glyphosate component may be used in its free acid form or in a salt form, such as as the isopropylamine salt or a sodium salt, ammonium salt or a potassium salt. Any salt of glyphosate which in aqueous solution provides glyphosate anions and suitable cations can be used in this invention. Examples of such cations are alkali metal or earth-alkali-metal cations; for instance sodium and potassium, and ammonium and substituted ammonium cations. The latter include cations derived from primary or secondary amines such as isopropylamine or dimethylamine, and from diamines such as ethylenediamine. US Patent 3,799,758 discloses glyphosate salts useful in this invention. Other examples of agriculturally acceptable salts of glyphosate are trimethylsulfonium salt or aminoguanidine salts as disclosed in EP-A-0 088 180. Because glyphosate has more than one replaceable hydrogen atom, mono- and di- alkali metal salts are possible, as well as mixtures of such salts.

The inorganic ammonium salt is an essential feature rendering the compositions suitable for further processing, particularly granulation. The ammonium salt can be ammonium thiocyanate, ammonium phosphate, ammonium carbonate, ammonium nitrate or ammonium chloride but is preferably ammonium sulfate. The content of ammonium salt may range from 20% to 80% of the total weight of the composition.

The composition according to the invention is usually to be diluted in water before being sprayed or applied in another known manner on the plant species to be treated. The dilution may be such that conventional spraying of 100-600 l/ha provides 0.125 to 1.5 kg of glyphosate acid equivalent per hectare. Spray solutions for controlled drop spraying are more concentrated.

The phytoactivity of herbicidal compositions inter alia also depends on the quantity of glyphosate used for treating the particular plant species; thus, the quantity of composition used is always expressed in gram glyphosate acid equivalents per hectare. It has been found that 200-600 grams acid equivalent per hectare have provided the most significant results.

The invention will be described in more detail hereafter, based upon the following Examples.

Example 1

Preparation of the formulation according to the invention

Glyphosate acid of technical purity is mixed with alkyl polyglycoside surfactant, ammonium sulfate (and inerts).

- 5 According to a first embodiment an acid acceptor (NaOH, NH_4HCO_3 , KOH, $(\text{NH}_4)_2\text{HPO}_4$, trisodium citrate) is reacted with glyphosate acid to form the corresponding salt. Depending on the acid acceptor, carbon dioxide and water may be generated from the reaction and water can possibly be evaporated if the reaction is exothermic. According to another embodiment, glyphosate acid may be used directly.
- 10 The desired ingredients are mixed together in order to prepare a pasty mixture convenient for producing water soluble granules by techniques like fluid bed granulation, extrusion, spray-drying, pan granulation, etc. Alternatively the mixture may be compressed into tablets or briquettes of any desired size and shape. Extrusion, and particularly radial extrusion, is a suitable agglomeration process. It has been found that by radial extrusion, a product with much better dissolution characteristics in water can be obtained, compared with a product prepared by frontal extrusion.
- 15 After final drying following extrusion, the granules may be sieved to avoid the presence of lumps or dust. A composition of the invention was:

- glyphosate sodium salt (100%)	22.29% w/w
- Atplus 258 surfactant (100%)	9.86
- $(\text{NH}_4)_2\text{SO}_4$ (100%)	59.19
- impurities	0.67
- NaOH excess	0.23
- DC 24 10	0.06
- water	7.69
% w/w = percent weight per weight.	

In the following examples, the immediately above composition bears the reference numeral 2.
Another composition according to the invention is exemplified hereafter:

- glyphosate sodium salt	30.34% w/w
- Atplus 450 surfactant	5.37%
- ammonium sulfate	59.85%
- impurities	1.79%
- MSA defoamer	1.16%
- water	1.50

Example 2

Greenhouse evaluation on geranium molle at different formulations according to the invention.

- 45 The dry formulations of this invention were dissolved in water and sprayed by a Mardrive sprayer on the test plant species at a temperature of 12°/18° C and relative humidity of 65%/75% day/ night.

	Formulation No.	Surfactant used	Ratio Gly a.e./surf./AS
5	0 (control)*	ethoxylated fatty amine	2 / 1 / 0
	1 (invention)	Atplus 258	2 / 1 / 8
	2 (invention)	Atplus 258	2 / 1 / 6
10	3 (control)	Atplus 258	2 / 1 / 0

The results obtained are shown in Table 1.

15 * = aqueous formulation of isopropylamine salt of glyphosate with
ethoxylated fatty amine surfactant.

20 Formulation 1 also contains a glyphosate sodium salt and the Atplus 258 surfactant, such as formulation 2,
but in a different ratio.

Control (3) is a liquid formulation of glyphosate isopropylamine salt and Atplus 258 surfactant without
ammonium sulfate.

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TABLE 1Percent phytotoxicity obtained on geranium

Formulation No.	glyphosate g.a.e./Ha*	% phytotoxicity	
		at day 16	30
0	200	22	50
	400	42	75
	600	40	80
	800	50	84
1	200	33	58
	400	52	80
	600	65	90
	800	63	95
2	200	27	50
	400	42	78
	600	55	86
	800	55	92
3	200	17	45
	400	33	68
	600	58	84
	800	58	90

*g.a.e./Ha = grams acid equivalent per hectare.
at day 16 = 16 days after treatment.

Example 3Greenhouse evaluation on rape

The same formulations as those used in Example 2 have been sprayed on rape by a Mardrive sprayer, at a temperature of 12/18°C and relative humidity of 65%/75% day/night.
The results obtained are shown in Table 2.

TABLE 2Percent phytotoxicity obtained on rape

	Formulation	glyphosate	% phytotoxicity	
	No.	g.a.e./Ha	at day 16	30
10	0	200	22	30
		400	33	43
		600	47	59
15		800	63	58
	1	200	50	52
		400	50	50
20		600	68	63
		800	63	69
25	2	200	46	45
		400	54	59
		600	60	77
30		800	53	75
	3	200	38	30
		400	43	33
35		600	58	70
		800	60	69

Example 4Greenhouse evaluation on couch (Elymus repens)

45 The same formulations as those used in Examples 2 and 3 were sprayed on the above test plant species. After 21 days after treatment (DAT), the plants were cut at pot level, and regrowth was measured after 2 weeks. Test conditions: temperature of 12/18° C and relative humidity of 65%/75% day/night. The results obtained are shown in Table 3.

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TABLE 3

Percent phytotoxicity and percent regrowth obtained on rape					
Formulation	glyphosate	% phytotoxicity		% regrowth	
No.	g.a.e./Ha	14	21	35	DAT
0	200	17	10	55	
	400	35	50	18	
	600	35	52	15	
	800	42	60	11	
1	200	35	58	4	
	400	50	75	4	
	600	50	79	3	
	800	55	85	1	
2	200	28	52	9	
	400	51	67	4	
	600	50	78	2	
	800	60	85	1	
3	200	25	38	14	
	400	38	57	12	
	600	40	63	5	
	800	45	67	2	

40 Example 5

Plants were grown from seed in 10 cm pots containing a natural sandy loam soil. The pots were placed in a growth-room until the spraying with a precise relative humidity as well as temperature control. After spraying plants were transferred into a greenhouse where light and temperature were also well controlled.

45 Plants remained in this greenhouse for the remainder of the experiment. Both in the growth-room and in the greenhouse, the water was supplied from below the pots by an automatic irrigation system.

Plants reached the appropriate growth stage for spraying around 3-4 weeks after sowing. Before spraying, pots were selected for uniformity as far as possible and atypical pots were discarded.

A composition according to the present invention comprising isopropylamine salt of glyphosate, an alkyl polyglycoside and ammonium sulphate in the weight ratio 2:1:6 was diluted with water and sprayed with a

50 Mardrive sprayer at a spray volume of 200 l/ha on oilseed rape (BRSNW), couch (AGRRE), lolium (LOLRI) and geranium (GERMO). All replicate pots (3 pots per treatment) were sprayed with one pass of the sprayer.

Pots were distributed randomly in the greenhouse after treatment. Untreated control pots were placed at

55 random among treated pots.

Assessment of per cent phytotoxicity was made by comparison with untreated control pots on an arbitrary scale from 0 to 100%, where 0 means no visible effect and 100 means death of all plants.

Tank mixed formulations according to the present invention are compared with liquid compositions

containing no inorganic ammonium salt.

The results were assessed at 14 days, 22 days and 35 days after treatment.

In the following table "GLYPHOSATE IPA" means a liquid composition containing the isopropylamine salt of glyphosate.

TABLE 4

Compo- sition	Application rate g.a.e./ha	BRSNW			AGRRE			LOLRI			GERMO		
		DAT			DAT			DAT			DAT		
		14	22	35	14	22	35	14	22	35	14	22	35
GLYPHOSATE IPA ATPLUS 450	200	10	7	17	52	57	53	33	28	20	27	27	28
GLYPHOSATE IPA ATPLUS 450	400	30	22	40	62	63	78	55	82	75	52	65	57
GLYPHOSATE IPA ATPLUS 450	600	67	75	75	58	73	70	52	75	72	62	68	55
GLYPHOSATE IPA ATPLUS 450 AMS (2:1:6)	200	12	13	15	40	43	40	40	27	20	28	25	43
GLYPHOSATE IPA ATPLUS 450 AMS (2:1:6)	400	65	67	67	57	65	65	68	97	98	67	82	78
GLYPHOSATE IPA ATPLUS 450 AMS (2:1:6)	600	60	62	63	62	72	73	67	92	95	80	83	78
GLYPHOSATE IPA ATPLUS 258	200	30	48	22	47	25	40	38	32	40	23	33	18
GLYPHOSATE IPA ATPLUS 258	400	48	62	60	53	63	65	65	83	82	47	68	47

Compo- sition	Application BRSNW			AGRRE			LOLRI			GERMO		
	rate			DAT			DAT			DAT		
	g.a.e./ha			14	22	35	14	22	35	14	22	35

GLYPHOSATE IPA 600 73 77 78 70 80 87 72 93 97 60 77 70
ATPLUS 258

GLYPHOSATE IPA 200 23 28 25 53 53 45 42 53 28 35 57 37
ATPLUS 258
AMS (2:1:6)

GLYPHOSATE IPA 400 60 62 57 57 63 68 70 92 83 60 78 68
ATPLUS 258
AMS (2:1:6)

GLYPHOSATE IPA 600 75 77 73 73 85 75 77 95 95 82 92 83
ATPLUS 258
AMS (2:1:6)

From Table 4 even on weeds difficult to control by glyphosate, like oilseed rape and couch, the compositions according to the present invention show effective activity at the rates applied. On more easily controlled weeds, like Lolium or Geranium, at the highest application rate, the activity is boosted by the presence of ammonium sulfate.

Example 6

A further composition of the invention is exemplified hereafter:

- glyphosate sodium salt	42.43% w/w
- APG 300 (Henkel)*	4.50%
- Dodigen 4022 (Hoechst) (propoxylated quaternary ammonium)	10.50%
- ammonium sulfate	40.09%
- impurities	0.96%
- MSA defoamer	0.33%
- water	0.25%

*alkyl polyglucoside

This composition has been diluted with water and sprayed at 200 l/ha in a single pass using standard field spraying equipment.

The rates of application were equivalent to 360, 720 and 1440 g glyphosate acid equivalent per hectare.

Weeds assessed: Geranium molle (GERMO)
Matricaria chamomilla (MATCH)
Poa annua (POANN).

The treatment was carried out in November. The temperature at spraying was about 14 °C. Heavy night frost (about -10 °C) was recorded during the week following the spraying. No rain was recorded during that time.

Assessment of per cent phytotoxicity was made by comparison with untreated control plots on an arbitrary scale of 0 to 100%, where 0 means no visible effect and 100 means death of all plants.

TABLE 5

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Composition	rate g a.e/ha	GERMO 26 DAT	MATCH 26 DAT	POANN 26 DAT
*Control	360	12	32	37
	720	30	40	50
	1440	40	43	62
Composition	360	22	32	43
of this	720	27	42	53
Example	1440	33	42	55
*Control = isopropylamine salt of glyphosate + ethoxylated fatty amine surfactant (Roundup® herbicide).				

The example shows that under the conditions of this test, the efficacy of the composition of this example was comparable to a current commercial glyphosate composition containing an ethoxylated fatty amine surfactant.

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From the above Examples 1-5 the formulations according to the invention are comparable to and in some tests more active than a commercial composition which as sold does not contain any ammonium sulfate but which comprises a different surfactant, an ethoxylated fatty amine.

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Due to the physico-chemical properties of the constituents used in the above compositions, ammonium sulfate is an essential constituent for obtaining the desired dry formulations in an acceptable manner allowing further processing by extrusion, spray bed drying, pan granulation, fluid bed agglomeration, etc.

Claims

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1. A solid phytoactive composition comprising:

- a) N-phosphonomethylglycine in the form of a salt or the acid;
- b) an alkyl glycoside or alkyl polyglycoside; and
- c) an agriculturally acceptable inorganic ammonium salt, preferably ammonium sulfate.

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2. A composition according to Claim 1 characterized in that the ratio by weight of glyphosate acid equivalent to alkyl polyglycoside is between 1:1 and 10:1.

3. A composition according to Claim 1 or Claim 2 characterized in that the alkyl glycoside or alkyl polyglycoside is used alone or in combination with one or more other surfactants.

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4. A composition according to Claim 3 characterized in that the other surfactant is a sorbitan ester, quaternary ammonium, or amine surfactant.

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5. A composition according to Claim 3, wherein said salt of N-phosphonomethylglycine is the isopropylamine salt or the trimethylsulfonium salt.

6. A composition of Claim 5, wherein said salt is the isopropylamine salt.

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7. A composition according to any of the preceding claims characterized in that the content of inorganic ammonium salt is between 20% and 80% of the total weight of the composition.

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8. Method for controlling unwanted vegetation which comprises applying to a plant to be treated, a phytotoxic amount of a composition according to any of Claims 1-7, diluted in water in order to apply between 0.125 and 1.5 kg glyphosate acid equivalent per hectare.

9. A process for preparing the composition of any one of Claims 1-7 by reacting an acid acceptor with glyphosate or using glyphosate directly and mixing said alkyl glucoside or alkyl polyglucoside and ammonium sulfate therewith in order to prepare a pasty mixture and thereafter granulating, extruding or spray drying to prepare said composition.



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 91 87 0020

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	EP-A-0 364 202 (ICI AUSTRALIA LTD) ---		A 01 N 57/20 //
D,A	EP-A-0 220 902 (STAUFFER CHEMICAL CO.) ---		(A 01 N 57/20 A 01 N 43:16 A 01 N 59:02 A 01 N 25:12 A 01 N 25:30)
A	WO-A-9 007 275 (MONSANTO CO.) ---		
A	DERWENT CHEMICAL PATENTS INDEX, BASIC ABSTRACTS JOURNAL, section C: AGDOC, week 8736, 4th November 1987, accession no. 87-253854/36, Derwent Publications Ltd, London, GB; & JP-A-62 175 408 (ISHIHARA SANGYO KAISHA) 01-08-1987 ---		
A	EP-A-0 206 537 (STAUFFER CHEMICAL CO.) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			A 01 N
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 03-10-1991	Examiner DONOVAN T.M.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			